

Chapter 3

**THE APPLICATION OF HEADSPACE:
SOLID-PHASE MICROEXTRACTION
(HS-SPME) COUPLED WITH GAS
CHROMATOGRAPHY/MASS SPECTROMETRY
(GC/MS) FOR THE CHARACTERIZATION
OF POLYMERS**

Peter Kusch*

Hochschule Bonn-Rhein-Sieg, University of Applied Sciences,
Department of Applied Natural Sciences, Rheinbach, Germany

ABSTRACT

Solid-Phase Microextraction (SPME) is a very simple and efficient, solventless sample preparation method, invented by Pawliszyn and co-workers at the University of Waterloo (Canada) in 1989. This method has been widely used in different fields of analytical chemistry since its first applications to environmental and food analysis. SPME integrates sampling, extraction, concentration and sample introduction into a single solvent-free step. The method saves preparation time, disposal costs and can improve detection limits. It has been routinely used in combination with gas chromatography (GC) and gas chromatography/mass

* Corresponding Author address Email: peter.kusch@h-brs.de.

spectrometry (GC/MS) and successfully applied to a wide variety of compounds, especially for the extraction of volatile and semi-volatile organic compounds from environmental, biological and food samples.

Since the last twenty years, SPME in headspace (HS) mode is used as a valuable sample preparation technique for identifying degradation products in polymers and for determination of rest monomers and other light-boiling substances in polymeric materials. For more than ten years, our laboratory has been involved in projects focused on the application of HS-SPME-GC/MS for the characterization of polymeric materials from many branches of manufacturing and building industries. This book chapter describes the application examples of this technique for identifying volatile organic compounds (VOCs), additives and degradation products in industrial plastics, rubber, and packaging materials.

Keywords: HS-SPME, GC/MS, polymers, volatile organic compounds (VOCs), identification

INTRODUCTION

Sample preparation is an essential step in analysis, greatly influencing the reliability and accuracy of resulted time and cost of analysis. Most of modern sampling methodologies for chromatographic analysis involve one of the basic mass transfer processes, alone or in combination: partition (where analytes are removed from samples by dissolution in a proper solvent), adsorption (the analyte are bonded or retained over the solid surface) and volatilization (volatile target species are selectively vaporized and separated from the matrix and interfering compounds) [1]. Solid-Phase Microextraction (SPME) is a very simple and efficient, solventless sample preparation method, invented by Pawliszyn and co-workers at the University of Waterloo (Canada) in 1989 [2-4]. This method has been widely used in different fields of analytical chemistry since its first applications to environmental and food analysis. SPME integrates sampling, extraction, concentration and sample introduction into a single solvent-free step. Solutes from a sample are directly extracted into an absorptive polymeric layer coated onto a solid fused silica fiber. After some time of exposure of fiber to the sample, equilibrium is reached and the extracted mass is, from this moment on, maximized and constant. The amount of extracted analytes is proportional to their concentration in the sample. Then the SPME fiber and captured solutes are transferred into an injection-system that desorbs the solutes into a gas mobile phase (helium) of the gas

chromatograph (GC). At the same time the analysis run is started. The method saves preparation time, disposal costs and can improve detection limits. It has been routinely used in combination with gas chromatography (GC) and gas chromatography/mass spectrometry (GC/MS) and successfully applied to a wide variety of compounds, especially for the extraction of volatile and semi-volatile organic compounds from industrial, environmental, biological and food samples [5].

Since the last twenty years, SPME in headspace (HS) mode is used as a valuable sample preparation technique for identifying degradation products in polymers and for determination of rest monomers and other light-boiling substances in polymeric materials [6-12]. For more than ten years, our laboratory has been involved in projects focused on the application of HS-SPME-GC/MS for the characterization of polymeric materials from many branches of manufacturing and building industries. This book chapter describes the application examples of this technique for identifying volatile organic compounds (VOCs), additives and degradation products in industrial plastics, rubber, and packaging materials.

Principles of SPME

In SPME, a small amount of the extracting phase associated with a solid support is placed in contact with the sample matrix for a predetermined amount of time. If the time is long enough, concentration equilibrium is established between the sample matrix and the extraction phase. When equilibrium conditions are reached, exposing the fiber for a longer amount of time does not accumulate more analytes [13]. The amount of solute in the SPME layer at equilibrium ($M_{i,SPME}$) can be approximated by the following equation 1:

$$M_{i,SPME} \sim K_{i,SPME} V_{SPME} C_i \quad (1)$$

where $K_{i,SPME}$ is an aggregate solute distribution constant between the SPME absorptive layer and the sample, V_{SPME} is the volume of the SPME layer, and C_i is the solute concentration in the sample before performing SPME sampling [14]. Equation 1 assumes that the sample volume is much greater than the volume of the SPME layer. SPME coatings typically have thicknesses of about 10-100 μm typically around 10 times the film thickness range normally encountered in capillary GC columns. Standard SPME layers, with smaller

volumes, would imply correspondingly smaller minimum sample volumes [14]. SPME coatings can be classified primarily into four categories: by the type of coating, by the coating thickness, by polarity and by whether the coating is an absorbent or an adsorbent [15]. A listing of commercial fibres available from Supelco is shown in Table 1 [15, 19]. The type of phase applied determines the polarity of the coating. Polarity can provide selectivity by enhancing the affinity of the coating for polar analytes compared to a non-polar fibre coating. Essentially, all SPME fibres are bipolar to some degree because they will extract both polar and non-polar analytes [15].

Table 1. Summary of commercially available SPME fibres [15, 19]

Fibre coating	Film thickness (µm)	Polarity	Coating method	Maximum operating temperature (°C)	Technique	Compounds to be analysed
Polydimethylsiloxane (PDMS)	100	Non - polar	Non-bonded	280	GC/HPLC	Volatiles
Polydimethylsiloxane (PDMS)	30	Non-polar	Non-bonded	280	GC/HPLC	Non-polar semivolatiles
Polydimethylsiloxane (PDMS)	7	Non-polar	Bonded	340	GC/HPLC	Medium- to non-polar semivolatiles
PDMS–Divinylbenzene (DVB)	65	Bipolar	Partially cross-linked	270	GC	Polar volatiles
PDMS–Divinylbenzene (DVB)	60	Bipolar	Partially cross-linked	270	HPLC	General purpose
Polyacrylate (PA)	85	Polar	Partially cross-linked	320	GC/HPLC	Polar semivolatiles
DVB–Carboxen-PDMS	50/30	Bipolar	Highly cross-linked	270	GC	Odours and flavours
Carboxen–PDMS	75	Bipolar	Partially cross-linked	320	GC	Gases and volatiles
Carboxen–PDMS	85	Bipolar	Highly cross-linked	320	GC	Gases and volatiles
Polyethylene glycol (PEG) (Carbowax)	60	Polar	Partially cross-linked	250	HPLC	Surfactants
Carbowax–DVB	65	Polar	Partially cross-linked	265	GC	Polar analytes
Carbowax–DVB	70	Polar	Highly cross-linked	265	GC	Polar analytes

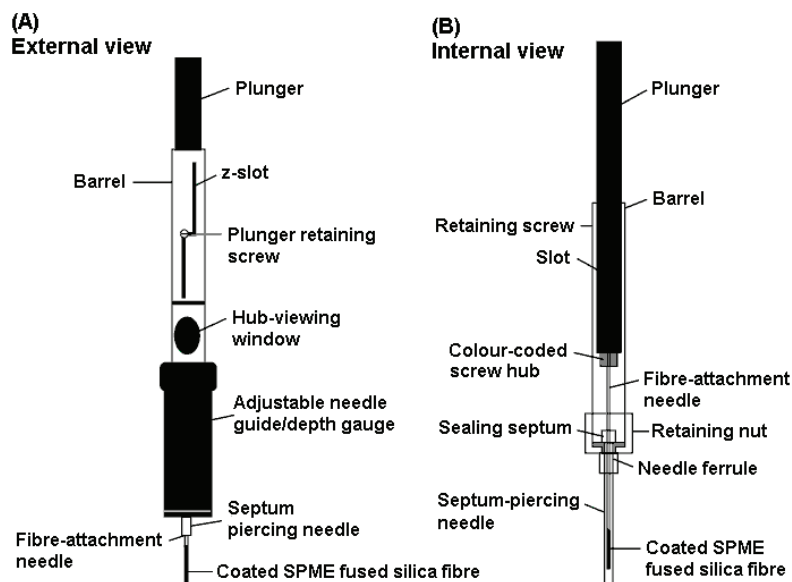


Figure 1. Schematic view of a SPME manual fibre assembly holder. Reprinted from [15] with permission from Elsevier.

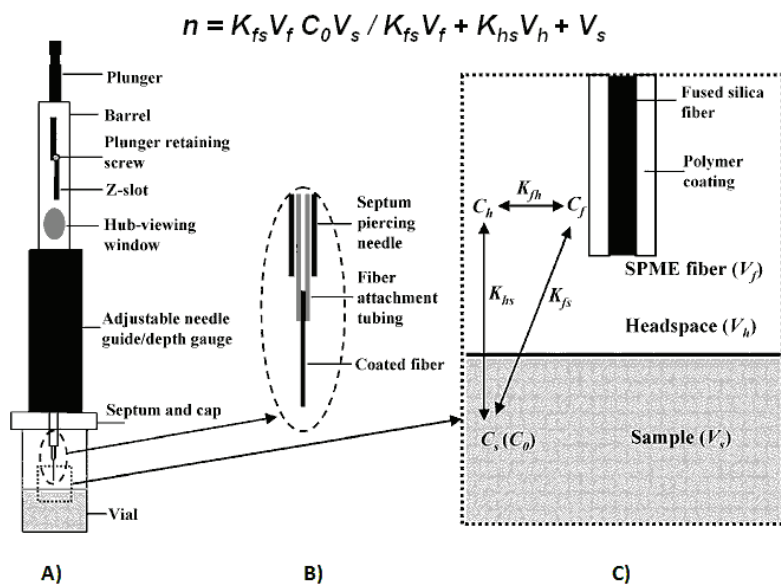


Figure 2. Schematic illustration of a SPME device. A) SPME device with sampling vial. B) Fiber assembly. C) Extraction mechanism in the three-phase system. Reprinted from [17] with permission from ACS.

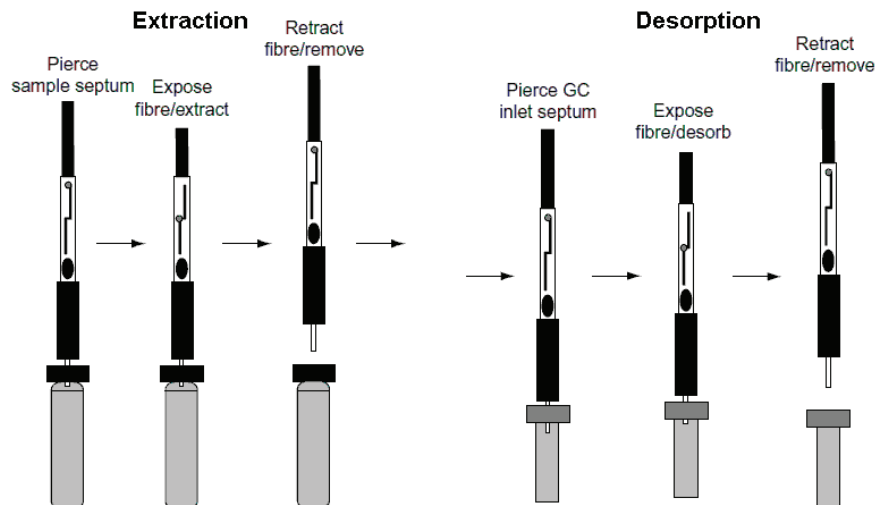


Figure 3. Steps of typical SPME extraction and thermal desorption in GC injector. Reprinted from [15] with permission from Elsevier.

Figures 1-2 show the schematic view of the first commercial version of the SPME manual fibre assembly holder (SPME device) introduced by Supelco in 1993 [15-19]. The manual holder has a z-slot to lock the fibre in the exposed position. When the plunger is unlocked, the fibre will retract into the needle if it is a manual assembly. The holder designed for autosamplers does not contain the needle guide depth gauge or the z-slot. It is simply a straight slot. The process of sampling is illustrated in Figure 3 [15]. The sample is placed in a glass vial, which is sealed with a septum-type cap. The new SPME fibre should be conditioned before using, and cleaned after analyzing. Cleaning can be done by inserting the fibre in an auxiliary hot injection port or by inserting into a syringe cleaner. When the SPME needle pierces the septum and the fibre is extended through the needle into the sample (Figure 3), partitioning between the sample matrix and the stationary phase takes place. This may occur in two different ways: headspace (HS-SPME) or direct immersion (DI-SPME). In HS-SPME, the fibre is exposed in the vapour phase above a gaseous, liquid or solid sample. In DI-SPME, the fibre is directly immersed in liquid samples. Agitation of the sample is often carried out with a small stirring bar for liquid samples or by sonication of solid samples for HS-SPME to decrease the time necessary for equilibration. For liquid polymeric SPME coatings, the amount of analyte absorbed by the coating at equilibrium

is directly related to the concentration of the analyte in the sample according to the equation 2 [16-18]:

$$n = K_{fs} V_f C_0 V_s / K_{fs} V_f + V_s \quad (2)$$

where:

n = mass of analyte absorbed by coating

C_0 = initial concentration of analyte in sample

K_{fs} = partition coefficient for analyte between coating and sample matrix

V_f = volume of coating

V_s = volume of sample

This equation shows that the relationship between the initial concentration of analyte in the sample and the amount of analyte absorbed by the coating is linear [16-18].

The mass of the analyte absorbed by the coating at equilibrium for HS SPME can be expressed as in the equation 3 [18]:

$$n = K_{fs} V_f C_0 V_s / K_{fs} V_f + K_{hs} V_h + V_s \quad (3)$$

where:

n = mass of analyte absorbed by coating

C_0 = the initial concentration of the analyte in the matrix

K_{fs} = the fibre/headspace distribution constant

K_{hs} = the headspace/sample distribution constant

V_f , V_h and V_s are the volumes of the coating, the headspace and the matrix, respectively.

After a suitable extraction time the fibre is withdrawn into the needle, the needle is removed from the septum and is then inserted directly into the hot injection port of the GC or GC/MS system (Figure 3). The analytes are thermally desorbed and transferred by a carrier gas to the capillary column. Desorption temperature must be high enough, so that the solutes rapidly leave the SPME fiber. A desorption that is too slow may lead to peak broadening and tailing unless additional arrangements are made for trapping solutes at the beginning of the GC column before temperature-programmed elution. Conversely, too high of an inlet temperature may induce thermal

decomposition and introduce some contaminants into the column from septum bleed, as well as from the SPME layer itself [14]. The HS- and DI-SPME techniques can be used in combination with any GC or GC/MS equipment [19].

EXPERIMENTAL

Samples

Samples (A and B) of commercially available expanded polystyrene (EPS, Styropor) and polyurethane packaging foam (PUR) from Germany, poly(acrylonitrile-*co*-1,3-butadiene-*co*-styrene)/polycarbonate (ABS/PC) and poly(acrylonitrile-*co*-1,3-butadiene-*co*-styrene)/polyamide-6 (ABS/PA 6) blends, car wrapping foils and rubber membranes from the hydraulic cylinders (all samples from the German automotive industry), as well as samples of poly(vinyl chloride) (PVC) floor covering from a day nursery were used for investigation.

Solid-Phase Microextraction (SPME)

The SPME fiber holder for manual use and the 75- μ m Carboxen-Polydimethylsiloxane (CAR/PDMS) fibers obtained from Supelco (Bellefonte, PA, USA) were used for extraction.

The fiber was conditioned at 300°C for one hour prior to first use. Twenty-milliliter headspace glass vials with an aluminum-coated silicone rubber septum and pressure released aluminium seal, obtained from LABC Labortechnik (Hennep, Germany) were used. A Sonorex Super RK 31H compact ultrasonic bath from Bandelin electronic (Berlin, Germany) was employed at 60°C for sample agitation.

SPME Procedure

Ca. 50 mg of the solid sample was sealed in a twenty-milliliter headspace glass vial with aluminum-coated silicone rubber septum. The septum of the vial was pierced with the needle of the SPME device and the fiber was exposed approximately 10 mm above the solid sample. Afterwards the glass

vial with the SPME injector was placed in an ultrasonic bath and agitated by sonication for 15 min at 60°C. After a sorption time of 15 min in the headspace above the sample, the fiber was retracted into the protective sheath and removed from the headspace glass vial. It was transferred without delay into the injection port of the gas chromatograph/mass spectrometer. The fiber was thermally desorbed in the injection port at 250°C for one minute and the GC/MS run was started.

Instrumentation and Analytical Conditions

A 7890A gas chromatograph (GC) with a series 5975C quadrupole mass spectrometer (MS) (Agilent Technologies Inc., Santa Clara, CA, USA) operated in electron impact ionization (EI) mode was used for measurements. The fused silica GC capillary column (30 m long, 0.25 mm I.D.) with DB-5MS UI stationary phase, film thickness 0.25 µm (J&W Scientific, Folsom, CA, USA) was used for chromatographic separations. Helium, grade 5.0 (Westfalen AG, Münster, Germany) was used as a carrier gas at constant flow of 1.1 cm³/min. The gas chromatographic conditions were as follows: programmed temperature of the capillary column from 60°C (1 min hold) at 7°C/min to 280°C (hold to the end of analysis); the temperature of the split/splitless injector was 250°C and the split ratio was 5:1.

The transfer line temperature was 280°C. The MS EI ion source temperature was kept at 230°C.

The ionization occurred with a kinetic energy of the impacting electrons of 70 eV. The quadrupole temperature was 150°C. Mass spectra and reconstructed chromatograms (TIC) were obtained by automatic scanning in the mass range m/z 35-750 u. GC/MS data were processed with the *ChemStation* software (Agilent Technologies) and the *NIST 05* mass spectral library.

RESULTS AND DISCUSSION

Among volatile monomers, residual solvents and impurities, the commercial plastics and rubbers always contain low-molecular-weight additives. These compounds are essential in polymer or copolymer processing and in ensuring the end-use properties of a polymer or copolymer. Additives can improve or modify the mechanical properties (fillers and reinforcements),

modify the color and appearance (pigments and dyestuffs), give resistance to heat degradation (antioxidants and stabilizers), provide resistance to light degradation (UV stabilizers), improve the flame resistance (flame retardants), improve the performance (antistatic or conductive additives, plasticizers, blowing agents, lubricants, mould release agents, surfactants, and preservatives) and improve the processing characteristics (recycling additives) of polymers or copolymers [20]. Some of the additives accumulate in the environment and affect our health and the environment. Knowledge of additives is important for evaluating the environmental impact and interaction of polymeric materials, investigating long-term properties and degradation mechanisms, verifying ingredients, investigating manufacturing problems, qualifying control polymeric materials, identifying odorants, avoiding workplace exposure and insuring safety of food packaging and medical products. Identification of polymer or copolymer additives is also desired if competitor products are investigated [20].

For about 15 years, our laboratory has been involved in projects from the area of failure analysis in the automotive, chemical or rubber industry by using the pyrolysis-GC/MS and headspace-SPME-GC/MS. The practical application of these analytical techniques ranges from case studies of automotive components failure analysis of failed hydraulic cylinders, membranes, as well as the packaging materials, sealing rings, tire materials and additives, to auto paints or auto wrapping foils. The obtained analytical results are then used for troubleshooting and remedial action of the technological process. Here, I report on application examples of the headspace-SPME-GC/MS method for identification of volatile organic compounds and additives in polymers and rubbers from packaging, automotive and domestic materials.

Identification of Volatile and Semivolatile Organic Compounds in Packaging Materials

Packaging is a major end-use for four primary plastics, as high-density polyethylene (HDPE), low-density polyethylene (LDPE), polypropylene (PP) and polystyrene (PS). Thermoplastic polyesters, such as bottle-grade poly(ethylene terephthalate) (PET), find extensive use in the soft-drink bottle market. Knowledge about the content of volatile residual solvents, monomers, and impurities or additives, for example, plasticizers and UV stabilizers, in such plastics is important if the material is used in the packaging of food, beverages, cosmetics or medicines. The substances may affect the quality of

products stored inside, if they migrate through the plastic. Because of problems with the direct gas chromatographic (GC) analysis of a polymer solution, the organic emissions from plastics are usually controlled by various hyphenated gas chromatographic techniques, for example, coupling of GC with headspace (HS) [21], with thermal desorption (TD) [22], with pyrolysis (Py) [20], and more recently, with solid-phase microextraction (SPME) [6-12, 23-26].

Expanded Polystyrene (EPS)

EPS is produced by polymerizing styrene monomer and adding *iso*-pentane as a blowing agent. It is used for food packaging and for protection of products against damage during transport and storage. EPS is also used in the building industry for insulation of exterior walls and foundations.

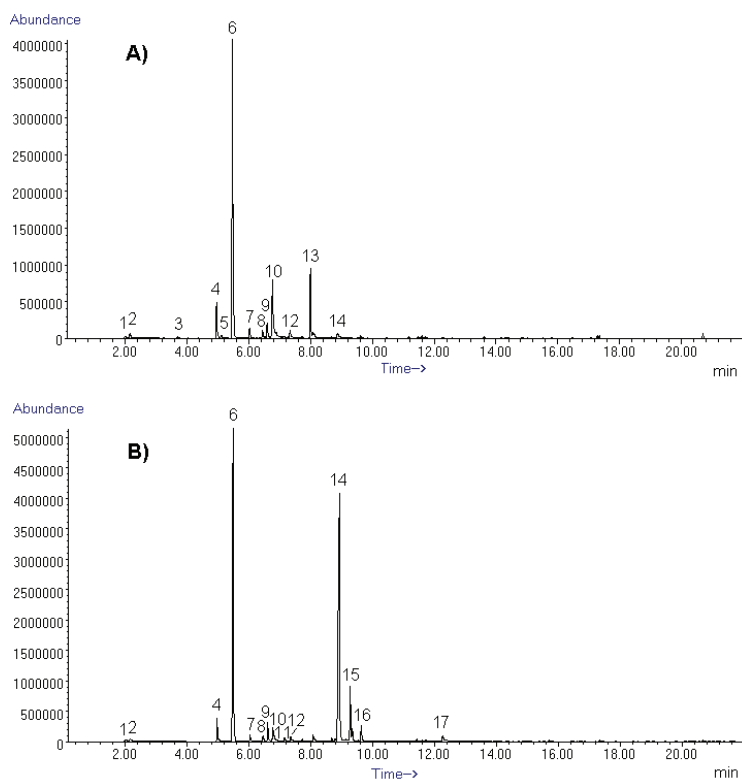


Figure 4. Total ion current GC/MS chromatograms (TIC) obtained from the headspace of two extracted EPS (expandable polystyrene) samples A and B.

Table 2. Volatile organic compounds released from expanded polystyrene (EPS) by headspace-SPME-GC/MS at 60°C

Peak No.	Retention time t_R [min]	Identified compound		CAS Number
		EPS sample A	EPS sample B	
1	2.02	Carbon dioxide	Carbon dioxide	124-38-9
2	2.17	2-Methylbutane	2-Methylbutane	78-78-4
3	3.71	Toluene		108-88-3
4	4.97	Ethylbenzene	Ethylbenzene	100-41-4
5	5.11	<i>p</i> -Xylene		106-42-3
6	5.48	Styrene	Styrene	79637-11-9
7	6.04	Cumene	Cumene	98-82-8
8	6.45	2-Propenylbenzene	2-Propenylbenzene	300-57-2
9	6.60	Propylbenzene	Propylbenzene	103-65-1
10	6.77	Benzaldehyde	Benzaldehyde	100-52-7
11	7.15		α -Methylstyrene	98-83-9
12	7.35	1-Ethenyl-2-methylbenzene	1-Ethenyl-2-methylbenzene	611-15-4
13	7.99	2-Ethyl-1-hexanol		104-76-7
14	8.90	Acetophenone	Acetophenone	98-86-2
15	9.28		Benzenemethanol	100-51-6
16	9.63		α -Methylbenzeneacetaldehyde	93-53-8
17	12.26		β -Methylenebenzeneethanol	6006-81-1

It has been known for a long time that EPS emits residual styrene monomer and other volatile organic compounds (VOCs) at ambient temperature. Styrene is harmful when inhaled, it is irritating to eyes, nose, throat, skin, and acts as a depressant on the central nervous system, causing neurological impairment [10, 11]. In my investigation, headspace-SPME followed by gas chromatography/mass spectrometry (GC/MS) has been applied to the identification of volatile organic compounds (VOCs) released from expanded polystyrene (EPS) at 60°C. Figure 4 shows typical total ion current GC/MS chromatograms (TIC) obtained from the headspace of two extracted EPS samples (A and B). Identification of compounds was carried out by comparison of retention times and mass spectra of standards, study of the mass spectra and comparison with data in the *NIST 05* mass spectral library. The retention data and the summarizing of the identification results are given in Table 2. As can be seen from Table 2, the headspace above the EPS samples contains residual styrene monomer, impurities of styrene such as alkyl

benzenes, and oxidation products, as well as residual 2-methylbutane (*iso*-pentane) used as a blowing agent by polymerizing of EPS. A part of the identified VOCs also can be formed by thermooxidative degradation of EPS when exposed to high temperatures and solar irradiation [11].

Polyurethane (PUR) Foam

Polyurethanes (PUR) are a large family of polymers whose composition has evolved over time. Polyurethane foams are largely used in automobiles, home furniture and thermal insulation. Approximately 13 kg of polyurethane foams are used in a car [27]. The applications range from seat cushions to headrests, instrument panel foams and headliners. Polyurethanes are also widely present in museum collections such as natural history museums, fine art museums, modern art museums, either as a part of the artefacts, or as a material for their conservation (stuffing, protection, packaging and storage) [25, 26]. Among museum collections they feature predominantly as sculptures, design objects, cushioning materials, textiles and toys [25, 26]. Polyurethane foams are regarded as potential causes of VOCs emissions.

Figure 5 shows the total ion current GC/MS chromatogram (TIC) obtained from the headspace of the investigated packaging polyurethane foam (PUR). The results of GC/MS identification are summarized in Table 3. As can be seen from Table 3, the low molecular weight compounds contain alkyl aldehydes and residual solvents, like tripropylene glycol monomethyl ether and tri(1,2-propylene glycol) monomethyl ether. Of the semivolatile organic compounds (SVOCs) phenolic antioxidants (2,6-di-*tert*-butyl-4-methylphenol and 3,5-di-*tert*-butyl-4-hydroxybenzaldehyde) were detected as well as plasticizers, like diisobutyl adipate and diethyl-, dibutyl- and diisobutyl phthalates. Phthalate esters are produced all over the world in large quantities for different uses. One important application is the use as a polymer plasticizer. The release of phthalates into the environment may occur during production and distribution and due to migration from polymeric materials [24]. Due to the widespread use, they have become common organic pollutants. In recent years, considerable attention has been paid to human exposure to phthalates because they are suspected to cause various health effects and possess carcinogenic and estrogenic properties [24, 28].

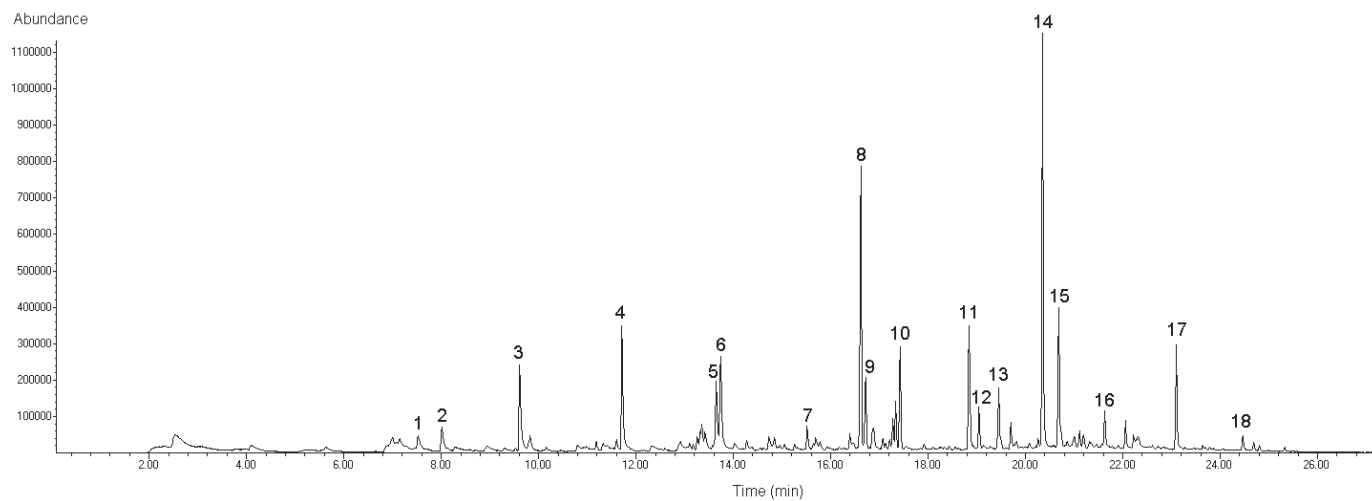

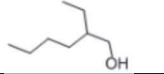


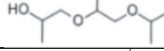
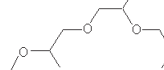

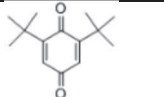
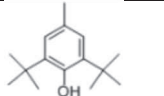
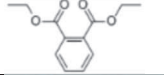

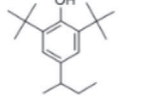
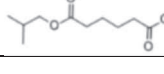
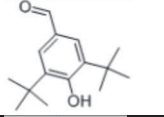
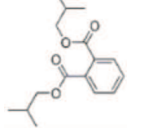
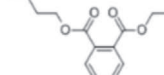


Figure 5. Total ion current GC/MS chromatogram (TIC) obtained from the headspace of the packaging polyurethane foam (PUR).

Table 3. Volatile and semi-volatile organic compounds released from polyurethane (PUR) foam by headspace-SPME-GC/MS at 60°C

Peak No.	Retention time t_R [min]	Identified compound	Chemical structure
1	7.53	1-Octanal	
2	7.99	2-Ethyl-1-hexanol	
3	9.62	1-Nonanal	
4	11.72	1-Decanal	
5	13.65	Tripropylene glycol monomethyl ether (Dowanol 62 b)	
6	13.74	Tri(1,2-propylene glycol) monomethyl ether	
7	15.50	<i>n</i> -Tetradecane	
8	16.62	Not identified	
9	16.70	2,6-Di- <i>tert</i> -butyl- <i>p</i> -benzoquinone	
10	17.41	2,6-Di- <i>tert</i> -butyl-4-methylphenol (BHT)	
11	18.83	Diethyl phthalate	
12	19.03	<i>n</i> -Hexadecane	
13	19.45	2,6-Di- <i>tert</i> -butyl-4- <i>sec</i> -butylphenol	
14	20.36	Diisobutyl adipate	
15	20.68	Not identified	
16	21.63	3,5-Di- <i>tert</i> -butyl-4-hydroxybenzaldehyde	
17	23.09	Diisobutyl phthalate	
18	24.45	Dibutyl phthalate	

Emission of Volatile and Semivolatile Organic Compounds from Polymers/Copolymers from the Automotive Industry

Plastic materials are viewed as the culprits for the VOCs emission in vehicle cabins. Material testing for outgassing volatile organic chemicals is required in many industries to ensure consumers are not being exposed to harmful contaminants. This is especially important when a material such as a plastic is exposed to excess heat with little or no ventilation. A good example would be plastic materials in a car such as dashboards, which are exposed to very high temperatures in direct sunlight.

For determination of volatile organic compounds in a variety of solid waste matrices the US EPA 8260B GC/MS method is used [29]. This method is applicable to nearly all types of samples, regardless of water content, including various air sampling trapping media, ground and surface water, aqueous sludges, caustic liquors, acid liquors, waste solvents, oily wastes, mousses, tars, fibrous wastes, polymeric emulsions, filter cakes, spent carbons, spent catalysts, soils, and sediments. The US EPA 8260B GC/MS method can be used to quantitate most volatile organic compounds that have boiling points below 200°C [29].

In this investigation, headspace-SPME-GC/MS method was used for the identification of volatile and semivolatile organic compounds in polymers/copolymers from the automotive industry. Some application examples are described below.

ABS/PC Blend

Poly(acrylonitrile-*co*-butadiene-*co*-styrene) (ABS) is a common thermoplastic used in light, rigid, and molded products such as automotive body parts, musical instruments, household appliances, toys, and food containers [30]. 1,3-Butadiene, acrylonitrile, and styrene are starting materials in the production of ABS. In general, synthetic polymers contain residual monomers, which remain in the polymers after the synthetic process. 1,3-Butadiene is classified as a carcinogen by the International Agency for Research on Cancer (IARC) and is a hazardous air pollutant. It is a potent classical alkylating agent and its metabolites are reactive compounds that form adducts with DNA or proteins [30]. Acrylonitrile is also believed to be carcinogenic. The acute toxicity of styrene has been well studied, being a skin and mucous membranes irritant and having narcotic properties [30]. Therefore, analysis of the trace residual monomers remained in this copolymer is needed.

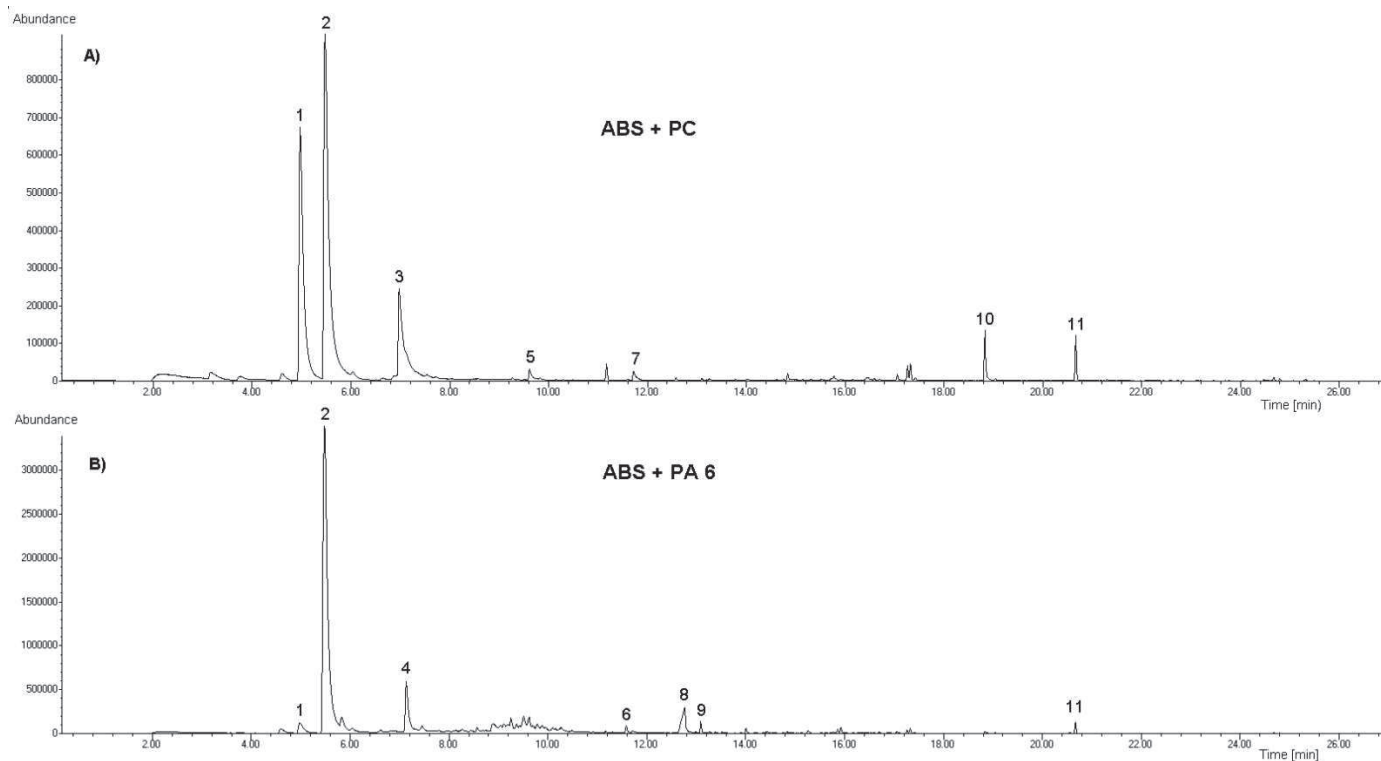


Figure 6. Total ion current GC/MS chromatograms (TIC) obtained from the headspace of the extracted A) ABS/PC blend, B) ABS/PA 6 blend from the automotive industry.

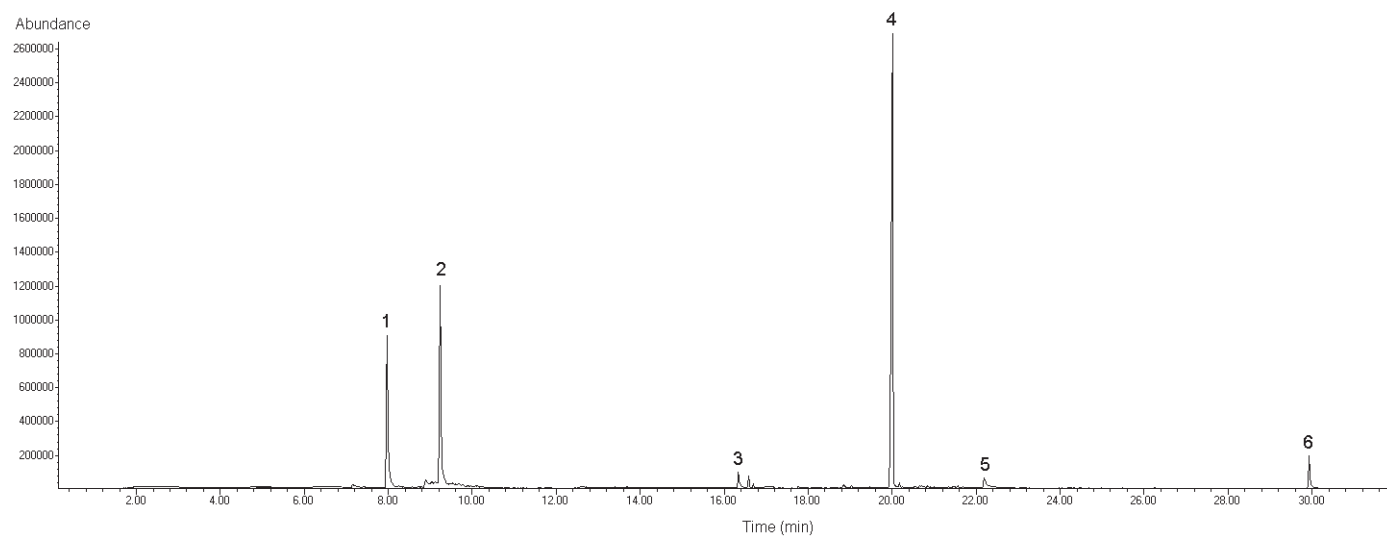
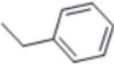
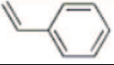
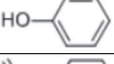
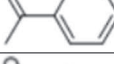

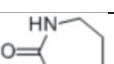

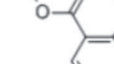
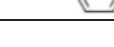


Figure 8. Total ion current GC/MS chromatogram (TIC) obtained from the headspace of the extracted rubber membrane from the hydraulic cylinder 1 from the automotive industry.

Table 4. Volatile and semi-volatile organic compounds released from ABS/PC und ABS/PA 6 blends from the automotive industry by headspace-SPME-GC/MS at 60°C

Peak N.	Retention time t_R [min]	Identified compound		Chemical structure
		ABS/PC	ABS/PA 6	
1	4.97	Ethylbenzene	Ethylbenzene	
2	5.48	Styrene	Styrene	
3	6.98	Phenol		
4	7.14		α -Methylstyrene	
5	9.62	1-Nonanal		
6	11.59		<i>n</i> -Tetradecane	
7	11.72	1-Decanal		
8	12.77		ϵ -Caprolactam	
9	13.10		<i>n</i> -Hexadecene	
10	18.83	Diethyl phthalate		
11	20.67	Not identified		

Polycarbonate (PC) is a clear and transparent, hard and ductile material. The great commercial success of bisphenol A polycarbonate (BPA-PC) is due to its unique combination of properties: extreme toughness, outstanding electrical insulation, transparency, good flame retardance, excellent compatibility with several polymers, and high heat distortion resistance. The electrical sector is the classical and major user of bisphenol A polycarbonate. Typical applications include housings for car telephones and distributor equipment, lamp sockets, relay parts, and components for electronic calculators. The building and construction industry has become the second most important user of polycarbonate [31]. Wall sheets from polycarbonates are used as roofs for green houses, halls, and bus- or railway stations. Polycarbonate is used in automobiles in light covers, reflectors, and fan or radiator grills. In optical information storage systems, special grade BPA-PC is used for production of audio/video compact discs (CD) [31]. This polymer is

widely used in reusable food packaging and in water and baby bottles. The migration studies concerned the migration of bisphenol A (BPA) from polycarbonate materials and information on other potential migrants. In the study by Nerin et al. [32] the extract from a commercial polycarbonate container consisted of a complex mixture containing monomers, oligomers, UV stabilizers, antioxidants and degradation products. In the method developed by Alin and Hakkarainen [33] headspace-SPME enabled extraction and identification of low molecular weight compounds migrating from PC containers during microwave heating in different food simulants. The migrants could be detected at low detection limits and all the compounds could be simultaneously quantified by using MHS-SPME (multiple headspace-SPME) or direct injection depending on the food simulant used. As an example 4-ethoxy-benzoic acid ethyl ester, 2,4-bis(1,1-dimethylethyl)-phenol and benzophenone had detection limits of 1, 0.1 and 3 ng/L respectively in water when extracted by the PDMS/DVB fibre.

In this work HS SPME-GC/MS was used for the identification of VOCs and SVOCs that were emitted from ABS/PC blend used in the automotive industry. Figure 6A shows the total ion current GC/MS chromatogram (TIC) obtained from the headspace of the extracted ABS/PC blend at 60°C. The identification results are summarized in Table 4. As can be seen from Table 4, the headspace above the ABS/PC blend contain residual styrene monomer and ethylbenzene (impurity of styrene) from ABS and phenol from thermal degradation of polycarbonate. Other of the emitted VOCs like 1-nonanal and 1-decanal may be formed by thermooxidative degradation of the blend when exposed to high temperatures and solar irradiation. The identified diethyl phthalate was used as plasticizer.

ABS/PA 6 Blend

Polyamides (PA) known as *nylons* are polymers that contain an amide group, -CONH-, as a recurring part of the chain. Polycaprolactam (PA 6) was the first polyamide made in an I. G. Farben (Germany) laboratory in 1938 by the hydrolytic polymerization of ϵ -caprolactam [31]. Today nylons are found in appliances, business equipment, electrical/electronic devices, furniture, hardware, machinery, packaging, and transportation. Transportation is the largest market for nylons. The softer nylons are used in fuel lines, air brake hoses, and coatings. Industrial applications are attracted to the excellent fatigue resistance and repeated impact strength of nylons. Examples are hammers and moving machine parts. Consumer products exploit the toughness

of nylons in ski boots, ice and roller skate supports, bicycle wheels, kitchen utensils, garden equipment, toys, and fishing lines [31].

Watanabe et al. [34] studied the thermal degradation of various plastics at various temperatures from 70 to 300°C under oxygen-present conditions to identify the semivolatile organic compounds (SVOCs) emitted and to understand their thermal behaviors. The plastics examined were nitrogen-containing polymers/copolymers, such as polyamide 6 (PA 6), polyurethane (PUR), melamine-formaldehyde resin, urea-formaldehyde resin and poly(acrylonitrile-*co*-1,3-butadiene-*co*-styrene) copolymer (ABS). ϵ -Caprolactam was the predominant compound in SVOCs emitted from PA 6 [34]. This chemical is known as a raw material of PA 6 and also as the major thermal-degradation product at high temperature.

Figure 6B shows the total ion current GC/MS chromatogram (TIC) obtained from the headspace of the extracted ABS/PA 6 blend from the automotive industry at 60°C. The identification results are summarized in Table 4. As can be seen from Table 4, the headspace above the ABS/PA 6 blend contain residual styrene monomer and ethylbenzene (impurity of styrene) from ABS and residual ϵ -caprolactam from PA 6. Also small amounts of *n*-alkanes, like *n*-tetradecane and *n*-hexadecane were detected in the headspace of ABS/PA 6 blend.

Car Wrapping Foils

The next objects of identification were car wrapping foils A and B. The plastic material of the investigated foil A was identified by pyrolysis-GC/MS in previous work of the author (P. K.) [35] as a mixture of flexible poly(vinyl chloride) (PVC) with bis(2-ethylhexyl) phthalate (BEHP) plasticizer and poly(hexamethylene adipamide) (Nylon 66). Figure 7A shows the obtained SPME-GC/MS total ion chromatogram (TIC) of the headspace (HS) of the extracted car wrapping foil A at 60°C. The identification results are summarized in Table 5. As can be seen from Table 5, the headspace above the car wrapping foil A (orange) contain alkyl alcohols (2-ethyl-1-hexanol, methyloctanol and 1-nonanol), 1-decanal, *p*-*tert*-butylbenzoic acid and dodecanoic acid. The identified 2-ethyl-1-hexanol is probably formed by thermal decomposition of bis(2-ethylhexyl) phthalate plasticizer. Furthermore, the antioxidant 2,6-di-*tert*-butyl-4-methylphenol (BHT) and its oxidized form 2,6-di-*tert*-butyl-*p*-benzoquinone were detected. The examined headspace above the car wrapping foil A contains some plasticizers, like diisobutyl adipate (fatty acid ester) and diethyl-, diisobutyl- and dibutyl phthalate (phthalate plasticizers).

Table 5. Volatile and semivolatile organic compounds released from car wrapping foil A (orange) by headspace-SPME-GC/MS at 60°C

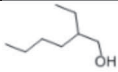



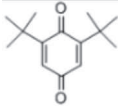
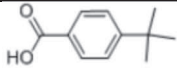
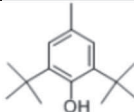

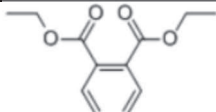
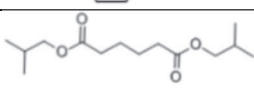
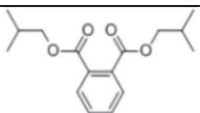
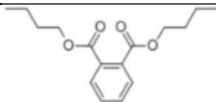



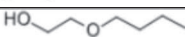



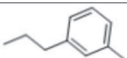


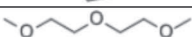
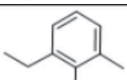
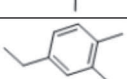
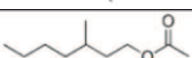
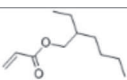

Retention time t_R [min]	Identified compound	Chemical structure
7.99	2-Ethyl-1-hexanol	
10.37	Methyloctanol	
10.97	1-Nonanol	
11.72	1-Decanal	
16.70	2,6-Di- <i>tert</i> -butyl- <i>p</i> -benzoquinone	
17.24	<i>p</i> - <i>tert</i> -Butylbenzoic acid	
17.41	2,6-Di- <i>tert</i> -butyl-4-methylphenol (BHT)	
18.43	Dodecanoic acid	
18.83	Diethyl phthalate	
20.34	Bis(2-methylpropyl) hexanedioate (Diisobutyl adipate)	
23.09	Diisobutyl phthalate	
24.45	Dibutyl phthalate	

Figure 7B shows the obtained SPME-GC/MS total ion chromatogram (TIC) of the headspace (HS) of the extracted car wrapping foil B (black) at 60°C. The identification results are summarized in Table 6. At 60°C the car wrapping foil B released various rest solvents like alkyl benzenes, 2-butoxyethanol, diethylene glycol dimethylether or 3-methylheptyl acetate. The

main component of the headspace above the foil B is the residual monomer 2-ethylhexyl acrylate (EHA) (retention time 12.16 min). 2-Ethylhexyl acrylate is a major base monomer for the production of acrylic adhesives. This adhesive is the main component of the analyzed car wrapping foil B.

Table 6. Volatile organic compounds released from car wrapping foil B (black) by headspace-SPME-GC/MS at 60°C

Retention time t_R [min]	Identified compound	Chemical structure
3.74	Toluene	
5.11	<i>p</i> -Xylene	
5.49	<i>o</i> -Xylene	
6.09	2-Butoxyethanol	
6.72	1-Ethyl-3-methylbenzene	
6.95	Phenol	
7.38	1,2,3-Trimethylbenzene	
8.53	1-Methyl-3-propylbenzene	
8.65	2-Ethyl-1,4-dimethylbenzene	
8.84	1-Methyl-4-propylbenzene	
8.97	Diethylene glycol dimethylether	
9.04	1-Ethyl-2,3-dimethylbenzene	
9.23	4-Ethyl-1,2-dimethylbenzene	
10.43	3-Methylheptyl acetate	
12.16	2-Ethylhexyl acrylate (EHA)	
15.50	<i>n</i> -Tetradecane	

Application of HS SPME-GC/MS in Failure Analysis in the Automotive Industry

Failure of the structure of materials or components often results in accidents and plant shutdowns, resulting in hefty compensations. Failure analysis is the process of collecting and analyzing data to determine the cause of a failure and to take action to prevent it from reoccurring [36]. It is an important discipline in many branches of manufacturing industry, such as the automotive industry and chemical or rubber industry. For the failure analysis in motor vehicles, there is often a lack of information about the component itself, such as chemical composition, temperature resistance, possible contaminants, or mechanical properties. The damage range is usually limited and not always homogeneous. There are often only small amounts of samples available to clarify the damage, which may be important for recognizing the cause of damage [36].

Commonly used rubbers in the automotive industry are natural rubber (NR, polyisoprene), synthetic polyisoprene (IR), polybutadiene (BR), styrene-butadiene copolymers (SBR) and nitrile rubber (NBR). Nitrile rubber [poly(acrylonitrile-*co*-butadiene)] is a copolymer containing 15 – 50% acrylonitrile, manufactured by emulsion polymerisation of acrylonitrile and 1,3-butadiene. It was invented at roughly the same time as SBR (near the end of the 1920s), as a substitute for natural rubber [37]. The major applications for this material are in areas requiring oil and solvent resistance. The largest market for nitrile rubber is in the automotive industry because of its solvent and oil resistance. Major end uses are for membranes, hoses, fuel lines, O-rings, gaskets and seals [37].

The goal of the study was to find the difference between the chemical composition of two different functioning rubber membranes from hydraulic cylinders from the automotive industry. Both investigated membranes were assigned by pyrolysis-GC/MS to nitrile rubber [poly(acrylonitrile-*co*-butadiene)] (NBR) based on the identified pyrolysis products [38]. Figures 8 and 9 show the obtained SPME-GC/MS total ion chromatograms (TIC) of the headspace (HS) of the extracted rubber membranes from the hydraulic cylinders 1 and 2 at 60°C, respectively. The identification results are summarized in Tables 7 and 8. As can be seen from Figure 8 and Table 7, triallyl isocyanurate (TAIC) was the main component of the headspace above the rubber membrane 1. TAIC is a crosslinking agent for improvement crosslinking efficiency by manufacturing of polymers and rubbers. The rubber obtained by using of TAIC has better mechanical

characteristics and larger heat-, hydrolytic- and weather resistance. Other compounds released from the rubber membrane 1 were 2-ethyl-1-hexanol (rest solvent or thermal degradation/hydrolysis product of bis(2-ethylhexyl) adipate plasticizer), α,α -dimethylbenzenemethanol, 1,2-dihydro-2,2,4-trimethylquinoline, phenanthrene and bis(2-ethylhexyl) adipate. 1,2-Dihydro-2,2,4-trimethylquinoline is used as an antioxidant in styrene-butadiene and nitrile-butadiene rubbers and latexes but the content of this substance in the headspace of the rubber membrane 1 was small (see Figure 8, peak 3). Bis(2-ethylhexyl) adipate (DEHA) is used as a plasticizer and as a functional hydraulic fluid. The main component in the headspace above the rubber membrane 2, however, was the antioxidant 3-*tert*-butyl-4-hydroxyanisole (BHA) (Figure 9, Table 8). Other rubber additives identified in the headspace of the rubber membrane 2 were benzothiazole, 1,2-dihydro-2,2,4-trimethylquinoline, antioxidant BHT and diethyl phthalate plasticizer (Figure 9, Table 8). The identified benzothiazole has been formed by the thermal degradation of 2-mercaptobenzothiazole. 2-Mercaptobenzothiazole is used as an accelerator for the vulcanisation of rubber and as an antioxidant.

Table 7. Volatile and semivolatile organic compounds released from rubber membrane from the hydraulic cylinder 1 from the automotive industry by headspace-SPME-GC/MS at 60°C

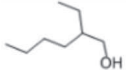
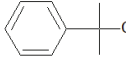
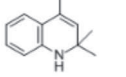
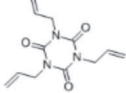

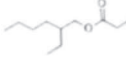






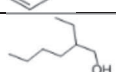
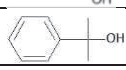



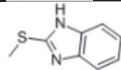
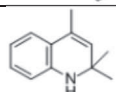
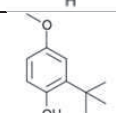
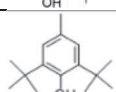
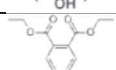
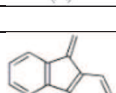
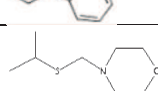
Peak No.	Retention time t_R [min]	Identified compound	Chemical structure
1	7.99	2-Ethyl-1-hexanol	
2	9.24	α,α -Dimethylbenzenemethanol	
3	16.34	1,2-Dihydro-2,2,4-trimethylquinoline (Vulkanox hs)	
4	20.01	Triallyl isocyanurate (TAIC)	
5	22.20	Phenanthrene	
6	29.93	Bis(2-ethylhexyl) adipate (Plasticizer DOA)	

Table 8. Volatile and semivolatile organic compounds released from rubber membrane from the hydraulic cylinder 2 from the automotive industry by headspace-SPME-GC/MS at 60°C

Peak No.	Retention time t_R [min]	Identified compound	Chemical structure
1	3.36	Methylisobutylketone	
2	4.04	1-Hexanal	
3	4.72	<i>tert</i> -Butylisothiocyanate	
4	4.97	Ethylbenzene	
5	5.48	Styrene	
6	6.77	Benzaldehyde	
7	7.99	2-Ethyl-1-hexanol	
8	9.24	α,α -Dimethylbenzenemethanol	
9	9.62	1-Nonanal	
10	11.72	1-Decanal	
11	12.30	Benzothiazole	
12	13.74	2-(Methylmercapto)-benzimidazol	
13	16.34	1,2-Dihydro-2,2,4-trimethylquinoline (Vulkanox hs)	
14	16.69	3- <i>tert</i> -Butyl-4-hydroxyanisole (BHA)	
15	17.41	Di-(<i>tert</i> -butyl)-4-methylphenol (BHT)	
16	18.83	Diethyl phthalate	
17	19.74	Not identified	
18	22.26	9-Methylene-9H-fluorene	
19	23.55	<i>N</i> -Morpholinomethyl-isopropyl-sulfide	

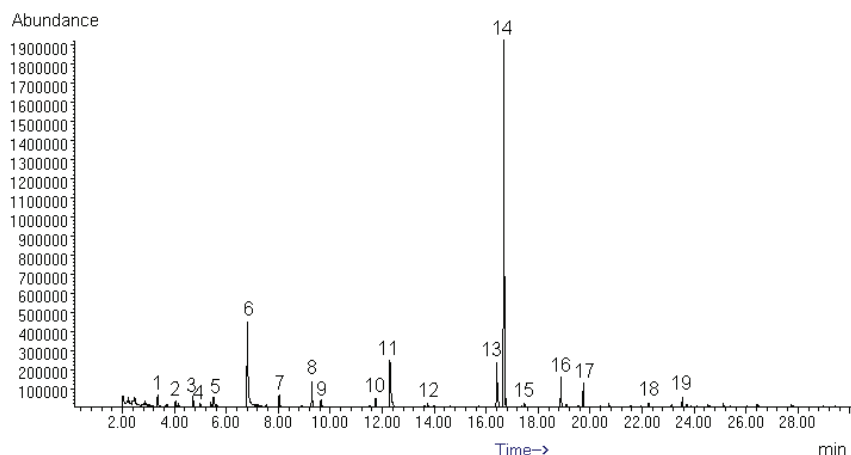


Figure 9. Total ion current GC/MS chromatogram (TIC) obtained from the headspace of the extracted rubber membrane from the hydraulic cylinder 2 from the automotive industry.

The observed differences in the functioning of the two rubber membranes 1 and 2 from hydraulic cylinders could be due different content of the identified rubber additives, like crosslinking agent, antioxidants and plasticizers.

Application of HS SPME-GC/MS for Identification of Vinyl Flooring Emission

The high sensitivity of SPME-GC-MS as a polymer analysis tool can be also demonstrated by identification of VOCs released from vinyl flooring (PVC). Vinyl flooring (VF) is manufactured in a variety of styles and compositions and is widely installed in residential and commercial buildings in either sheet or tile form [39]. VF is primarily composed of a mixture of poly(vinyl chloride) (PVC), inert filler (usually calcium carbonate, CaCO_3), and organic plasticizers such as dioctyl phthalate (DOP). Other additives such as stabilizers, lubricants, antioxidants, and colorants are used to aid in processing and improve product functionality and appearance [39]. VF may also be manufactured as a multi-layer system with a bottom backing (usually glass fiber) and a top coating of transparent PVC or polyurethane. In the United States during 1998, 214 million kilograms of PVC were used in the production of VF [39]. VF has been shown to emit a number of volatile

organic compounds (VOCs). VOCs can migrate from the interior to exposed surfaces by diffusion and then partition into the surrounding air. Most of the VOCs that are emitted by VF are probably present as contaminants in the various raw materials or as residues from the manufacturing process.

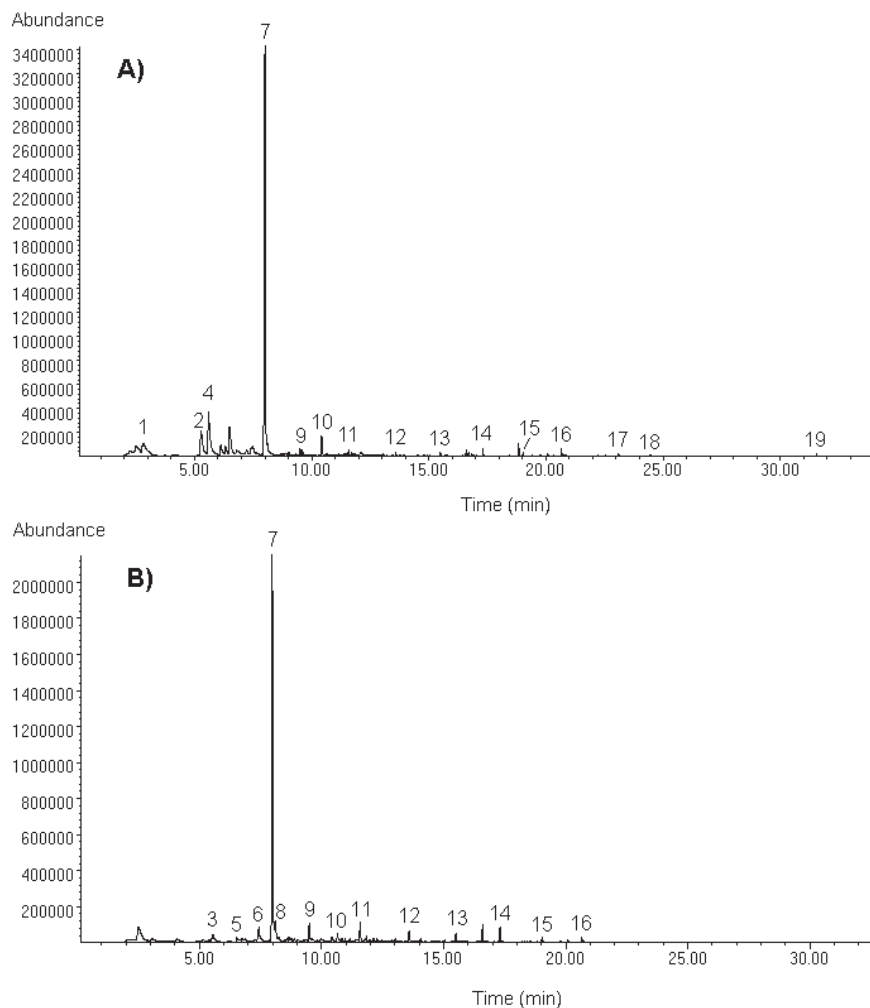

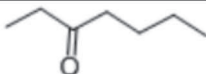


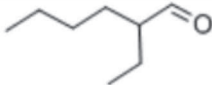

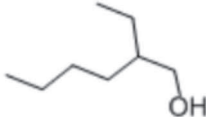
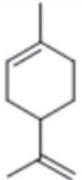

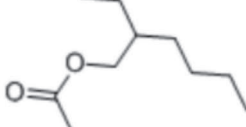






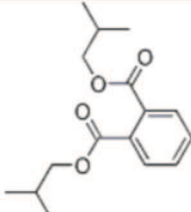
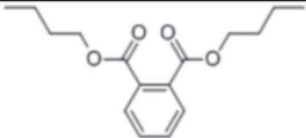
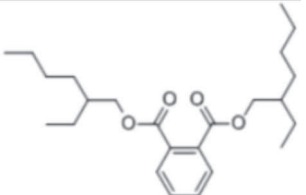


Figure 10. Total ion current GC/MS chromatograms (TIC) of substances emitted from A) PVC floor covering (vinyl flooring) and B) from the screed under the vinyl flooring from a day nursery.

Table 9. Volatile and semivolatile organic compounds released from PVC floor covering and from screed under the PVC floor covering from a day nursery by headspace-SPME-GC/MS at 60°C

Peak No.	t_R [min]	Identified compound		Chemical structure
		PVC floor covering	Screed under the PVC floor covering	
1	2.81	1-Butanol		
2	5.28	3-Heptanon		
3	5.54	<i>n</i> -Nonane		
4	5.60	2-Butoxyethanol		
5	6.54		2-Ethylhexanal	
6	7.43		<i>n</i> -Decane	
7	7.99	2-Ethyl-1-hexanol	2-Ethyl-1-hexanol	
8	8.10		Limonene	
9	9.50	<i>n</i> -Undecane	<i>n</i> -Undecane	
10	10.43	2-Ethylhexyl acetate	2-Ethylhexyl acetate	
11	11.58	<i>n</i> -Dodecane	<i>n</i> -Dodecane	
12	13.58	<i>n</i> -Tridecane	<i>n</i> -Tridecane	
13	15.50	<i>n</i> -Tetradecane	<i>n</i> -Tetradecane	
14	17.31	<i>n</i> -Pentadecane	<i>n</i> -Pentadecane	
15	19.03	<i>n</i> -Hexadecane	<i>n</i> -Hexadecane	
16	20.66	<i>n</i> -Heptadecane	<i>n</i> -Heptadecane	

Peak No.	t_R [min]	Identified compound		Chemical structure
		PVC floor covering	Screed under the PVC floor covering	
17	23.09	Diisobutyl phthalate		
18	24.45	Dibutyl phthalate		
19	31.55	Bis(2-ethylhexyl) phthalate		

The aim of the investigation was the identification of VOCs and SVOCs emitted from PVC floor covering (vinyl flooring) and from the screed under the VF covering from a day nursery by HS SPME-GC/MS at 60°C. The results of the identification are shown in Figure 10 and Table 9. As can be seen from Figure 10 and Table 9, 2-ethyl-1-hexanol was the main component emitted from PVC floor covering and from the screed under the VF covering. 2-Ethyl-1-hexanol is the rest solvent and/or thermal degradation product of the identified bis(2-ethylhexyl) phthalate plasticizer (Figure 10A, peak 19). Other identified rest solvents were 1-butanol, 3-heptanon, 2-butoxyethanol and 2-ethylhexyl acetate (Figure 10, Table 9). Other emitted substances from VF were diisobutyl- and dibutyl phthalate plasticizers. The presence of limonene and *n*-alkanes C_9H_{20} to $C_{17}H_{36}$ in the investigated headspace were associated with the cleaning and floor care products.

CONCLUSION

The headspace-SPME-GC/MS analytical method has been proven to be a valuable tool for the identification of volatile and semivolatile organic

compounds emitted from polymeric materials from many branches of manufacturing, building and automotive industries as well as in failure analysis in the automotive industry. The headspace-SPME technique can be introduced easily and quickly in every GC and GC/MS chemical laboratory.

ACKNOWLEDGMENTS

The author (P. K.) is grateful to his son Dipl.-Päd. Matthäus Kusch for his critical reading of the manuscript.

REFERENCES

- [1] De Oliveira A. M.; Pivato Biajoli A. F.; Vasconcelos Fidélis C. H.; Gomes da Costa Silva R.; Augusto F.; Extraction and pre-concentration techniques for chromatographic analysis. In: *Trends in Sample Preparation*; Arruda M. A. Z.; Ed.; Nova Science Publishers: New York, 2006; pp. 1-23.
- [2] Arthur C. L.; Pawliszyn J. Solid phase microextraction with thermal desorption using fused silica optical fibers. *Anal. Chem.* 1999, 62(19), 2145–2148.
- [3] Górecki T.; Pawliszyn J. Sample introduction approaches for solid-phase microextraction/rapid GC. *Anal. Chem.* 1995, 67(18), 3265–3274.
- [4] Pawliszyn J. *Application of Solid Phase Microextraction*; RSC: Cambridge, UK, 1999.
- [5] Vas G.; Vékey K. Solid-phase microextraction: a powerful sample preparation tool prior to mass spectrometric analysis. *J. Mass Spectrom.* 2004, 39, 233-254.
- [6] Hakkarainen M.; Karlsson S.; Albertsson A.-Ch. SPME as an effective means to isolate degradation products in polymers. *J. Environ. Polym. Degrad.* 1997, 5(2), 67-73.
- [7] Čížkova H.; Voldřich M.; Dobias J. Determination of residual acetaldehyde in polyethylene terephthalate bottles on SPME. *Czech J. Food Sci.* 1998, 16(4), 81-84.
- [8] Butinsky D.; Polowa K.; Sides S.; Thornquest A. Identification of pharmaceutical packaging off-odour using solid-phase microextraction-GC/MS. *J. Pharm. Biomed. Anal.* 2001, 25(3-4), 379-386.

-
- [9] Albertson A.-Ch.; Gröning M.; Hakkarainen M. Solid-phase microextraction (SPME) in polymer characterization. Long term properties and quality control of polymeric materials. *J. Appl. Polym. Sci.* 2003, 89(3), 867-873.
- [10] Kusch P.; Knupp G. Analysis of residual styrene monomer and other volatile organic compounds in expandable polystyrene by headspace solid-phase microextraction followed by gas chromatography/mass spectrometry. *J. Sep. Sci.* 2002, 25(8), 539-542.
- [11] Kusch P.; Knupp G. Headspace-SPME-GC-MS identification of volatile organic compounds released from expanded polystyrene. *J. Polym. Environ.* 2004, 12(2), 83-87.
- [12] Dutra C.; Pezo D.; De Alvarenga Freire M. T.; Nerín C.; Reyes F. G. Determination of volatile organic compounds in recycled polyethylene terephthalate and high-density polyethylene by headspace solid-phase microextraction gas chromatography-mass spectrometry to evaluate the efficiency of recycling processes. *J. Chromatogr. A.* 2011, 1218, 1319-1330.
- [13] Pawliszyn J. Theory of solid-phase microextraction. *J. Chromatogr. Sci.* 2000, 38(7), 270-278.
- [14] Majors R. E. *Sample Preparation Fundamentals for Chromatography*; Agilent Technologies Inc.: Wilmington, DE, USA, 2013, pp. 137-138.
- [15] Shirey R. E.; SPME commercial devices and fibre coatings. In: *Handbook of Solid Phase Microextraction*; Pawliszyn J.; Ed.; Elsevier: Amsterdam, 2012; pp. 99-132.
- [16] Supelco Bulletin 923; *Solid-phase microextraction: theory and optimization of conditions*; Supelco: Bellefonte, PA, USA, 1998.
- [17] Tang B; Isacson U. Analysis of mono- and polycyclic aromatic hydrocarbons using solid-phase microextraction: state-of-the-art. *Energy & Fuels* 2008, 22(3), 1425-1438.
- [18] Pawliszyn J.; Theory of solid-phase microextraction. In: *Handbook of Solid Phase Microextraction*; Pawliszyn J.; Ed.; Elsevier: Amsterdam, 2012; pp. 13-59.
- [19] Vas G.; Vékey K. Solid-phase microextraction: a powerful sample preparation tool prior to mass spectrometric analysis. *J. Mass Spectrom.* 2004, 39(3), 233-254.
- [20] Kusch P. Identification of organic additives in nitrile rubber materials by pyrolysis-GC-MS. *LCGC North America* 2013, 31(3), 248-254.
- [21] Kolb B.; Ettre L. S. *Static Headspace-Gas Chromatography. Theory and Practice*; Wiley-VCH: New York, USA, 1997.

- [22] Mitchell G.; Higgitt C.; Gibson L. T. Emissions from polymeric materials: Characterized by thermal desorption-gas chromatography. *Polym. Degrad. Stabil.* 2014, 107, 328-340.
- [23] Lerch O. Rapid automated screening of extractable compounds in materials for food packaging, medical or technical purposes. *Gerstel Application Note* 3/2012, pp. 1-11.
- [24] Hakkarainen M.; Solid phase microextraction for analysis of polymer degradation products and additives. In: *Advances in Polymer Science. Chromatography for Sustainable Polymeric Materials*; Albertsson A.-Ch.; Hakkarainen M.; Eds.; Springer-Verlag: Berlin, Heidelberg, 2008, volume 211; pp. 23-50.
- [25] Lattuati-Derieux A.; Egasse C.; Thao-Heu S.; Balcar N.; Barabant G.; Lavédrine B. What do plastics emit? HS-SPME-GC/MS analyses of new standard plastics and plastic objects in museum collections. *J. Cultural Heritage* 2013, 14(3), 238-247.
- [26] Lattuati-Derieux A.; Thao-Heu S.; Lavédrine B. Assessment of the degradation of polyurethane foams after artificial and natural ageing by using pyrolysis-gas chromatography/mass spectrometry and headspace-solid phase microextraction-gas chromatography/mass spectrometry. *J. Chromatogr. A* 2011, 1218(28), 4498-4508.
- [27] Mohd Azmil M. N.; Nurul'Ain H.; Razmah G.; Adnan S.; Kosheela Devi P. P.; Tuan Noor Maznee T. I.; Hazimah A. H. Determination of volatile organic compounds in palm-based polyurethane foams using static headspace gas chromatography mass spectrometer. *J. Oil Palm Research* 2015, 27(3), 273-281.
- [28] Report to the U.S. Consumer Product Safety Commission by the Chronic Hazard Advisory Panel on Phthalates and Phthalate Alternatives, U.S. Consumer Product Safety Commission Directorate for Health Sciences, Bethesda, MD 20814, July 2014.
- [29] US Environmental Protection Agency (EPA) Method 8260B *Volatile Organic Compounds by Gas chromatography/Mass spectrometry (GC/MS)*, December 1996.
- [30] Choi S.-S.; Kim Y.-K. Analysis of residual monomers in poly(acrylonitrile-co-butadiene-co-styrene). *Macromol. Research* 2012, 20(6), 585-589.
- [31] Kusch P.; Knupp G.; Morrisson A.; Analysis of synthetic polymers and copolymers by pyrolysis-gas chromatography/mass spectrometry. In: *Horizons in Polymer Research*; Bregg R. K.; Ed.; Nova Science Publishers: New York, 2005; pp. 170-175.

-
- [32] Nerín C.; Fernández C.; Domeño C.; Salafranca J. Determination of potential migrants in polycarbonate containers used for microwave ovens by high-performance liquid chromatography with ultraviolet and fluorescence detection. *J. Agric. Food Chem.* 2003, 51(19), 5647-5653.
- [33] Alin J.; Hakkarainen M. Migration from polycarbonate packaging to food simulants during microwave heating. *Polym. Degrad. Stabil.* 2012, 97, 1387-1395.
- [34] Watanabe M.; Nakata C.; Wu W.; Kawamoto K.; Noma Y. Characterization of semi-volatile organic compounds emitted during heating of nitrogen-containing plastics at low temperature. *Chemosphere* 2007, 68, 2063-2072.
- [35] Kusch P.; Knupp G.; Fink W.; Schroeder-Obst D.; Obst V.; Steinhaus J. Application of pyrolysis-gas chromatography-mass spectrometry for the identification of polymeric materials. *LCGC North America*, 2014, 32(3), 210-217.
- [36] Kusch P.; Schroeder-Obst D.; Obst V.; Knupp G.; Fink W.; Steinhaus J.; Application of pyrolysis-gas chromatography/mass spectrometry (Py-GC/MS) and scanning electron microscopy (SEM) in failure analysis for the identification of organic compounds in chemical, rubber, and automotive industry. In: *Handbook of Materials Failure Analysis with Case Studies from the Chemicals, Concrete and Power Industries*; Makhoul A. S. H.; Aliofkhazraei M.; Eds.; Elsevier: Amsterdam, 2016; pp. 441-469.
- [37] Kusch P.; Application of pyrolysis-gas chromatography/mass spectrometry in failure analysis in the automotive industry. In: *Automobiles and the Automotive Industry: Emerging Technologies, Environmental Impact and Safety Analysis*; Evans A. T.; Ed.; Nova Science Publishers: New York, 2015; pp. 41-64.
- [38] Kusch P.; Unpublished work. Hochschule Bonn-Rhein-Sieg, University of Applied Sciences, Rheinbach, Germany, 2010.
- [39] Cox S. S.; Hodgson A. T.; Little J. C. Measuring concentrations of volatile organic compounds in vinyl flooring. *J. Air & Waste Manag. Assoc.* 2001, 51(8), 1195-1201.